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SEVENTH INTERNATIONAL CONFERENCE ON AMORPHOUS  
AND LIQUID SEMICONDUCTORS AT EDINBURGH.

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10 S.G./BISHOP, T.L. REINECKE, U. STROM, P.C./TAYLOR  
C.C./KLICK

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\*Naval Research Laboratory, Washington, DC

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  A review is given of the Seventh International Conference on Amorphous and Liquid Semiconductors held in Edinburgh at the end of June 1977. Topics covered in the report include the nature of localized states in chalcogenide glasses, dispersive electronic transport, electronic conductivity at the Si-SiO <sub>2</sub> interface, amorphous Si and Ge, thermal and vibrational properties of amorphous solids, luminescence in oxide glasses, and disordered organic solids.  amorphous		

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SEVENTH INTERNATIONAL CONFERENCE ON AMORPHOUS AND  
LIQUID SEMICONDUCTORS AT EDINBURGH

The Seventh International Conference on Amorphous and Liquid Semiconductors was held in Edinburgh from 27 June to 1 July 1977. That it is the seventh conference tells us something of the age of this field of service; that the meetings have been biennial and well attended tells us something of its vigor and excitement. Perhaps some of the early workers entering the field of amorphous semiconductors anticipated that relatively minor modifications of the science of crystalline semiconductors would suffice for the understanding of this new field. That has certainly not been the case as the following pages testify. There have been major mysteries to unravel at the most fundamental levels. What are the defect centers in amorphous semiconductors? How is charge transported? What is the origin of the linear specific heat at low temperatures found in nearly all amorphous materials? Progress has been made on all of these problems, but final answers are still not with us. In the remainder of this report an attempt is made to summarize some of the progress that has been made as it was reported at the Conference.

A. LOCALIZED STATES IN CHALCOGENIDE GLASSES

Localized states in the gap of chalcogenide glasses were quite expectedly the focus of a considerable number of papers at this conference. The discussion of localized states has proceeded in the past few years from the general to the specific, unfortunately not necessarily as a consequence of increased understanding; specific situations are more easily accommodated than general principles! P.W. Anderson (Princeton Univ. and Bell Labs, notably absent from this Conference) originally proposed a model of doubly-occupied localized electronic states to explain the diamagnetic properties of chalcogenide glasses. The model was based on the suggestion that the polaron energy gained by the contraction of a bond more than compensates for the electron repulsion and an effective negative-correlation energy results. R.A. Street (Xerox, Palo Alto) and Prof. Sir Nevill Mott (Univ. of Cambridge, UK) applied Anderson's concept specifically to point defects (dangling bonds) and obtained a model which can be more directly related to experimental data. This model and the subsequent valence alternation pair (VAP) model of M. Kastner, D. Adler (MIT) and H. Fritzsche (Univ. of Chicago) utilize the interaction between nonbonding lone-pair electrons on different chalcogenide atoms and their local environment to generate localized states in the gap. In effect, extraordinary bonds are formed from the normally nonbonding orbitals giving rise to singly- and triply-coordinated chalcogen atoms in the VAP model.

These models and their implications for the interpretation of various experimental results concerning localized states were discussed in many of the papers presented at the Conference. In his invited opening address, Fritzsche reviewed the basic concepts of the Mott-Street (MS) and VAP models. Charged defects, formed in chalcogenide glasses, can be viewed as

either empty ( $D^+$ ), doubly-occupied ( $D^-$ ) dangling chalcogen bonds in the MS model, or as singly-coordinated ( $C_1^-$ ) and three-coordinated ( $C_3^+$ ) chalcogen atoms in the VAP model. Because of the negative effective-correlation energy for paired-electron (hole) states, singly-occupied states ( $D^0$ ) do not occur in equilibrium since the interaction  $2D^0 \rightarrow D^+ + D^-$  is exothermic. All defect centers are therefore either positively or negatively charged, and  $D^0$  occurs only by excitation (e.g., optical absorption). In the VAP terminology the preference for charged centers is expressed, for example, by the exothermic reaction  $2C_3^0 \rightarrow C_3^+ + C_1^-$ . Fritzsche pointed out that less energy is required to form a VAP than a single isolated defect. Just as valence alternation can produce singly- and three-coordinated atoms from the normally two-coordinated chalcogens, the normally three-coordinated pnictide atom (such as arsenic) in chalcogenide glasses could form charged defects by alternating between two and four coordination. These properties are unique to the chalcogenide glasses with their nonbonding orbitals since, for example, elemental amorphous group IV semiconductors cannot form VAPs because the five-coordinated state does not occur.

Fritzsche also discussed the concept of doping in chalcogenide glasses to change their defect-controlled properties. In the case of low-temperature doping where impurity atoms are introduced by diffusion below  $T_g$ , the number of VAPs that have come to equilibrium at  $T_g$  is not affected. If, for example, an impurity with excess electrons is introduced, these electrons convert  $C_3^+$  to  $C_1^-$ . If sufficient impurities are introduced to exceed the total number of VAPs, the excess impurity atoms can act as donors and move the Fermi energy toward the conduction band thereby yielding an appreciable increase in electrical conductivity. In the case of high-temperature doping, above  $T_g$ , the introduction of impurities can be made to generate new VAPs to satisfy the equilibrium conditions of charge neutrality and the law of mass action. The total VAP concentration could be made to increase by several orders of magnitude with attendant modification of defect-controlled physical properties of the glass.

An example of the effects of doping in chalcogenide glasses was provided in contributed papers by S.R. Ovshinsky and R. Flasck and coworkers (Energy Conversion Devices, Inc., Troy, MI). In the experiments reported, rf-sputtered thin films of chalcogenide glass alloys (typical composition:  $Ge_{32}Te_{32}Se_{32}As_4$ ) were "doped" by being cosputtered with dopants such as Ni, Fe, Mo, W, H, C. Ovshinsky pointed out that because of the high percentage of dopant introduced (~7-11%) the procedure might be more aptly termed "chemical modification." He also preferred to refer to the extraordinary bonding arrangements embodied in VAPs and  $D^0$ ,  $D^+$ ,  $D^-$  as "Deviant Electronic Configurations" (DECs). Annealed Ni-doped films exhibited extrinsic conductivity at room temperature and above, while possible  $T^{1/4}$  behavior was observed at low temperature. Electrical conductivity, optical absorption, and thermopower measurements were reported. Enormous increases in conductivity were produced by the Ni doping while the optical



measurements indicate that the energy gap remains essentially unchanged. Ovshinsky *et al* believe that only a small fraction of the Ni is electrically active. They point out that they had obtained similar results by doping sputtered Si in the same manner without including the hydrogen that occurs in glow-discharge deposited amorphous Si. Attempts to carry out similar doping in bulk glasses have been unsuccessful. The rapid quenching inherent in the sputtering process is apparently essential to the production of these compositions and effectively to "freeze" the VAP density (as described by Fritzsche).

One of the principal architects of the VAP model, Marc Kastner (MIT), expanded upon some of the concepts touched upon by Fritzsche in his opening address. From consideration of the energetics of the formation of unusual bonding configurations in chalcogenide glasses, he demonstrated that bond breaking results in the formation of three-coordinated chalcogens because dangling bonds are energetically unstable. The interaction between the positively and negatively charged centers of VAPs may or may not lead to the formation of intimate (closely spatially correlated) pairs (IVAPs) depending upon the strength of the interaction and the law of mass action. However, the coexistence of intimate and nonintimate pairs was shown to be very unlikely; i.e., there is no "gray" area, the pairs will be either all VAPs or all IVAPs.

The experimental evidence that prompted the models based on charged, radiative recombination centers (Ds and VAPs) comes from photoluminescence (PL) studies of various chalcogenide glasses. These charged-defect models have sought to explain various features of the luminescence such as the large Stokes shift, the excitation spectrum, the temperature dependence, and the photoluminescence decay or fatigue during continuous excitation. The highlights of this work were discussed in an invited review paper on optically induced localized states in chalcogenide glasses by S.G. Bishop, U. Strom, and P.C. Taylor (Naval Research Laboratory, Washington, DC). Bishop explained how it was determined that the PL excitation spectra provided the prescribed optical wavelengths for an optically activated process in which charged, diamagnetic radiative recombination centers in chalcogenide glasses are converted to electrically neutral, paramagnetic, radiatively inactive centers. He described how the fatigue of PL efficiency in chalcogenide glasses during optical excitation in the Urbach tail is paralleled by the growth of an optically induced electron-spin-resonance (ESR) spectrum and an optically induced mid-gap absorption. It was concluded that two types of optically induced paramagnetic centers occur in arsenic-chalcogenide glasses: holes localized in nonbonding chalcogen p-orbitals and electrons localized predominantly in arsenic p-orbitals. After briefly describing the temperature and composition dependences of the various optically induced effects, Bishop discussed the experimental results in terms of the MS ( $D^+D^-$ ) and VAP models. He concluded by suggesting that compositional trends in the photosensitivity to the fatiguing process might depend upon the tendency of the charged centers to form IVAPs

rather than isolated VAPs. In addition, the temperature dependence of the thermal quenching of the optically induced states could be explained on the basis of the pairing of states rather than a uniform spatial distribution.

C. Benoit à la Guillaume, F. Mollet, J. Cernogora, and M. Ben Soussan (Univ. of Paris VII) also reported studies of optically induced localized paramagnetic states in the chalcogenide-glass system  $\text{Ge}_x\text{Se}_{1-x}$ . Their results are qualitatively similar to those of Bishop *et al* with respect to the nature of the optically induced effects observed. However, while Bishop *et al* found that the density of optically induced paramagnetic centers saturates at or below  $10^{17} \text{ cm}^{-3}$  for all glasses studied (including  $\text{GeSe}_2$ ), the French workers interpreted their data as representative of densities of centers as high as  $10^{20} \text{ cm}^{-3}$ . Interestingly, in the case where the entire sample is excited by the inducing light, and the sample thickness defines the excited volume, Benoit *et al* agree with Bishop and coworkers. The French workers obtain their high densities for highly-absorbed exciting light ( $\alpha d \gg 1$ ) where  $1/\alpha$  is much less than the sample thickness and the determination of the saturated density is problematic. Benoit *et al* suggest that two different types of ESR centers are involved. This important suggestion requires resolution since conventional wisdom associates the saturated density of optically induced spins with the density of some defect or charged center in the glass, and  $10^{20} \text{ cm}^{-3}$  is rather high for the density of such defects.

Another interesting contributing paper in the luminescence session was that of S.J. Hudgens and M. Kastner (MIT) in which they presented evidence from PL-fatigue studies of chalcogenide glasses for the diffusion of elementary excitations. They studied the effects of fatiguing upon the shape of the PL-excitation spectrum for various wavelengths of fatiguing light. For deeply penetrating fatiguing light the entire PL-excitation spectrum is uniformly reduced in efficiency by the fatiguing process, and as expected, for more highly absorbed fatiguing light which cannot fatigue centers lying deeper than about  $1/\alpha$  in the sample, the high-energy portion of the excitation spectrum is selectively fatigued while the portion corresponding to more penetrating light is unfatigued. The remarkable feature of the data is that for very highly absorbed light  $1/\alpha \ll 1 \mu\text{m}$ , the glass is still fatigued to an apparent depth much greater than  $1/\alpha$ . Hudgens and Kastner suggest that this can be explained by the diffusion of the fatiguing species of excitation (e.g., an exciton) over distances as great as  $0.5 \mu\text{m}$ .

In what was apparently the only nuclear-magnetic-resonance (NMR) paper in the Conference, G.E. Jellison, Jr. and S.G. Bishop (Naval Research Laboratory, Washington, DC) reported that the nuclear-spin-lattice relaxation rate for thallium nuclei in arsenic-chalcogenide glasses can be enhanced by the optically induced localized paramagnetic states discussed above. In addition, studies of the temperature dependence of the spin-lattice



relaxation time,  $T_1$ , revealed a temperature regime where  $T_1$  is controlled by a thermally activated density of localized carriers. The conclusion that the thermally activated relaxation centers are localized was based on the observation that the relaxation process proceeds by nuclear-spin diffusion. Nuclei in the immediate vicinity of the localized centers are efficiently relaxed by a Fermi contact interaction, but the more remote volume of the sample depends upon spin diffusion for relaxation. Analyses of the data indicated that the relaxation centers are localized over dimensions less than about  $10 \text{ \AA}$ . The interpretation of the NMR data thus provides a unique method of determining the extent of localization of these thermally activated carriers.

The session on photostructural effects in chalcogenide glasses was highlighted by the paper of K. Tanaka and coworkers (Electrochemical Laboratory, Tanashi, Tokyo). Tanaka described the first determination of the spectral response or reversible photostructural change accompanying photodarkening (photoinduced red shift of the absorption edge) in  $\text{As}_2\text{S}_3$  glass. The measurements, carried out at room temperature, showed that light with photon energy greater than  $2.4 \text{ eV}$  ( $\alpha \geq 10^3 \text{ cm}^{-1}$ ) and as high as  $3.1 \text{ eV}$  shifts the absorption edge toward lower energies most efficiently, while irradiation with light for which  $\alpha < 10^2 \text{ cm}^{-1}$  produces no discernible optical and structural change. This spectral range of photostructural sensitivity contrasts with the spectral range of maximum sensitivity for optically induced paramagnetic states in chalcogenide glasses that is highest for  $\alpha \leq 10^2 \text{ cm}^{-1}$ . These results have important consequences regarding the relationship between the defect-related optically induced paramagnetism and the photostructural effects that involve a much larger fraction of the atomic sites on the glass. While both processes likely involve rearrangements of nonbonding chalcogen orbitals, they certainly have markedly different excitation spectra emphasizing the fundamental differences between the two processes.

R.A. Street (Xerox, Palo Alto) presented a contributed paper in which he associated the efficient nonradiative recombination mechanism known to exist in chalcogenide glasses with the reversible photostructural effects that occur. He asserted that the only mechanism that can satisfactorily account for the nonradiative release of  $\sim 2 \text{ eV}$  of excitation energy at a rate faster than the radiative rate is that of strong electron-phonon coupling. In his model a localized electron that is strongly coupled to the lattice lowers its energy (becomes self-trapped) by a bond-switching reaction that creates an intimate VAP. The energy released is easily large enough to make the recombination nonradiative. Furthermore, the  $\text{D}^+\text{D}^-$  pair that is formed contributes a metastable state that can only be reversed by heating. This effect could explain reversible photostructural changes and the associated photodarkening in chalcogenide glasses. Street pointed out that the model has the interesting property that the tendency to self-trap is much stronger for the exciton than for the individual electron and hole (that occur if the exciton ionizes) because unlike the neutral exciton, a charged carrier cannot form a  $\text{D}^+\text{D}^-$  pair.

Prof. N.F. Mott (Univ. of Cambridge, UK) presented an invited paper entitled "Silicon-Dioxide and Chalcogenide Semiconductors Compared and Contrasted." He extended and expanded a theme that he began at the Symposium on the Structure of Non-Crystalline Materials which was held in Cambridge, September 1976. Mott pointed out that just as a hole in the lone-pair orbital (nonbonding) of a chalcogen can form a bond with a neighboring chalcogen and the two atoms pull together, it is possible that the same thing will happen for a free hole in the valence band, and that a polaron or self-trapped hole would thereby be formed. He then suggested that such self-trapped holes are formed in  $\text{SiO}_2$  but not in chalcogenide glasses (e.g.,  $\text{As}_2\text{Se}_3$  and  $\text{As}_2\text{Te}_3$ ). In addition, because of the potential barrier that must be overcome for this type of trapping to occur, there is a considerable delay after excitation before self-trapping happens. Mott interpreted the so-called "prompt mobility" observed in  $\text{SiO}_2$  as attributable to such a delay before self-trapping. While electrons are not trapped and exhibit a high mobility, electron-hole pairs (excitons) may also be self-trapped (as discussed by R.A. Street) in  $\text{SiO}_2$  and chalcogenides. Again, the barrier for self-trapping results in a delay time.

Mott then discussed some optical absorption data pointing out that narrow-exciton absorption is expected for a free exciton and that the sharp feature at 10.2 eV in  $\text{SiO}_2$  is ascribed to such a free exciton. In contrast, the absorption line of a localized center (such as a self-trapped exciton) is broadened; in that case the broad absorption attributed to nonbridging oxygen associated with sodium ions in  $\text{Na}_2\text{O-SiO}_2$  glasses was cited. He stated that these nonbridging oxygens have properties similar to charged dangling bonds in chalcogenide glasses.

Finally, Mott discussed the recombination mechanism for free electrons and holes in  $\text{SiO}_2$  and chalcogenide glasses. He invoked the self-trapped exciton mechanism of Dexter, Klick, and Russel [*Phys. Rev.* 100, 603 (1955)] to explain the nonradiative nature of the dominant recombination mechanism. On the basis of Mott's brief concluding statement, one felt that the concept of delayed self-trapping was the substance which he would like the audience to carry away.

T.L. Reinecke (Naval Research Laboratory, Washington, DC, paper by Economou *et al*) described theoretical work on a novel physical mechanism for the origin of paired-electron and paired-hole states in  $\alpha$ -semiconductors that is based on the interaction between carriers and the tunneling modes characteristic of these materials. This mechanism is physically distinct from those proposed previously, and it also gives rise to singly-localized carriers and to mass enhancement of carriers at band edges as required by experiment. This work gives a detailed formulation for the calculation of (pair) binding energies, which has been given for other mechanisms.



## B. DISPERSIVE TRANSPORT

Extensive work on dispersive transport in amorphous solids was reported. Such transport (at moderately low temperatures  $\leq 150$  K) has common characteristics for a wide variety of disordered systems. G. Pfister (Xerox, Webster, NY) presented an invited paper (Pfister and Sher) in which he reviewed a wide variety of experimental results and made a detailed comparison with the stochastic-transport theory of Sher and Montroll.

Typically these experiments monitor the time dependence of the arrival of current at one face of a thin film after flash photoexcitation of the opposite face and under a constant electric field perpendicular to the film. (See ESN 31-8:320 for a more detailed description of this technique.) Experiments on a variety of inorganic amorphous materials including  $\alpha$ -Se,  $\alpha$ -As<sub>2</sub>Se<sub>3</sub>, and  $\alpha$ -SiO<sub>2</sub>, and organics such as PVK and TNF-PVK were reported. At moderately low temperatures the time dependence of the current is universally in marked contrast to what is expected from the statistical spreading of a Gaussian-carrier distribution. Specifically, (1) the current arrives with a time dependence  $I(t) \propto t^{-n}$  for  $t \leq t_T$  and  $I(t) \propto t^{-m}$  for  $t \geq t_T$ , where  $n + m \approx 2$  and  $t_T$  is a time characterizing the pulse arrival; (2) when normalized to  $I(t_T)$  and plotted as a function of  $1/t_T$ , the current for a variety of materials falls on a universal curve; and (3) the mobility is found to be dependent on the sample thickness. These dependences are in striking contrast to Gaussian behavior, and the weak dependence of  $I(t)$  on time suggests the existence of trapping and related processes with long delay times.

This behavior of the dispersive transport is, however, in good agreement with the predictions of the stochastic "continuous-time random-walk" formulation of dispersive transport of Sher and Montroll. The Sher-Montroll approach is a very general description which considers carrier transport subject to a succession of trapping or hopping "events" that have a very broad spectrum of "characteristic times" extending up to the transport time itself. If the distribution of characteristic times has the form  $\sim t^{-\alpha}$ ,  $0 < \alpha < 1$ , the resulting current can be shown to have the form given above with  $n = 1 - \alpha$  and  $m = 1 + \alpha$ , in a good agreement with experiment. The "universality" of the  $I(t)$  behavior for various materials and the thickness dependence of the mobility are also given by this theory. It should be noted carefully that because the microscopic origin of the trapping or hopping processes is not specified in the Sher-Montroll approach, this approach and its comparison to experiment does not normally give information about such mechanisms but only indicates that they have a wide statistical distribution.

Pfister went on to point out that preliminary experimental evidence suggests that the mechanism of "trap-controlled hopping" probably takes place in  $\alpha$ -As<sub>2</sub>Se<sub>3</sub>, whereas either "multiple trapping" or "hopping" are probably important in  $\alpha$ -Se. In a similar vein in a contributed paper, J.

Noolandi (Xerox, Ontario) discussed the solution of a set of rate equations for "multiple-trapping hopping" in which each trap is characterized by both a capture and a release rate. This approach is formally similar to the general approach of Sher and Montroll, and Noolandi showed that the results with suitable parameters could be used to fit data for  $\alpha$ -Se.

H. Sher (Xerox, Webster, NY) in a contributed paper, discussed how the Sher-Montroll approach can be particularized to show the dependence of the current on specific parameters of the traps, and he compared several such possibilities to experiment for mixed molecularly doped polymers and for  $\alpha$ -As<sub>2</sub>Se<sub>3</sub>.

M. Silver (Univ. of North Carolina) discussed numerical simulation work that raised some doubt whether simple hopping can account for dispersive transport.

In a slightly different vein, the distinguished theorist V.L. Bonch-Bruевич (Moscow Univ.) discussed the effects of the finite lifetime of discrete levels in the gap on the conductivity of amorphous materials. He pointed out, for example, that such discrete states contribute to the dc conductivity at  $T = 0$  only if they have finite lifetimes. He also commented on the rather different question of the existence of a "Coulomb gap" in amorphous materials and the conditions required for its existence.

#### C. CONDUCTIVITY AT THE Si-SiO<sub>2</sub> INTERFACE

A new feature of this Conference, as compared to previous ones, was a discussion of electron localization in the inversion layer formed at the Si-SiO<sub>2</sub> interface in the Si-MOS (metal-oxide semiconductor) configuration, which is an area of much current scientific and also technological interest. An inversion layer is formed by placing a potential bias between the metal (gate) and the silicon, thus creating a strong electric field at the Si-SiO<sub>2</sub> interface that leads to quantized levels for electronic motion in the Si perpendicular to the interface—that is, to an effective "two-dimensional electron gas" along the interface. The oxide is amorphous—particularly so at the interface—and thus the electrons in the Si inversion layer move in a random potential field due to the oxide. The conductivity of an inversion layer in a field-effect transistor formed from such an MOS device is an especially powerful technique for the study of electron localization and of the charges and the structures in the oxide causing localization. Conductivity can be varied from metallic conductivity to an activated regime in the same device by changing the gate voltage which also results in a change of the Fermi energy. Also, the spatial extent of the wave function can be altered by changing the bias, and the nature of the interface can be changed by altering fabrication techniques.

There has been much work in recent years on the electronic properties of inversion layers, and M. Pepper (Cambridge Univ. and The Plessey Co.,



Ltd.) presented an invited paper in which he reviewed much of the experimental work, especially that of the Cambridge group. He described a variety of low-temperature measurements of the activation energy and "minimum metallic conductivity" for systems in which density and substrate bias were varied and in some cases where radiation treatment was used.

Pepper concentrated on the important issue of how these measurements can be used to give information concerning the charges and the charge states in the oxide-causing localization. In particular he discussed evidence for the idea that many, but not all, of the charges near the interface exist in "compensated" pairs with net dipoles. Evidence for such a model includes: (1) the total number of carriers that are localized is larger than the net oxide charge (which is always positive and  $\sim 10^{11} \text{ cm}^{-2}$ ), and (2) the activation energy is always smaller than the binding energy to a single-charged center. When the extent of the electron-wave function perpendicular to the interface is altered, e.g., increased, by changing the bias at constant electron density, the "minimum metallic conductivity" increases and the activation energy decreases; Pepper argued that these effects could be understood on the basis of his picture of charged dipoles near the interface because as the electron-wave function moves farther from the interface, it then feels potential fluctuations of longer range. (We might parenthetically point out that a physically distinct explanation of these effects and of several other observations that is based on the idea of the existence of a novel kind of dynamic state of paired electrons at the interface has recently been proposed [K.L. Ngai and T.L. Reinecke, Naval Research Laboratory, *Phys. Rev. Lett.* 37, 1418 (1977)].)

Pepper also discussed the charge states resulting from hole transport to the interface upon radiation treatment and how these states can be investigated by studying the inversion-layer conductivity. Such interface charge-states that are enhanced by irradiation include the "slow states" within the oxide and the "fast states" in the Si band gap which are of technological interest. He cited evidence to suggest tentatively that the "slow states" are associated with the dipole-like pairs at the interface and the fast states may be associated with a Si dangling bond.

#### D. TETRAHEDRALLY COORDINATED AMORPHOUS SEMICONDUCTORS (MAINLY Si AND Ge)

The original impetus that caused the field of amorphous semiconductors to expand rapidly in the late 1960s and early 1970s was the promise of using chalcogenide glasses as competitive electronic devices for switching and memory applications. Most of this original impetus has long since abated, but this year's Conference produced renewed optimism for device possibilities in a slightly different area. This time the interest concerned the doping of amorphous Ge and Si and the use of these materials for solar-energy conversion [W.E. Spear and P.G. Le Comber, *Solid State Commun.* 17, 1193 (1975) from the University of Dundee; E.E. Carlson and

C.W. Wronski, *Appl. Phys. Lett.* **28**, 671 (1976) from RCA Laboratories, Princeton]. Several significant questions concerning these materials were effectively answered during this meeting while a few remain controversial.

The first experiments on doped amorphous Si and Ge were all performed using materials deposited by the electrical decomposition (rf-glow discharge) of silane ( $\text{SiH}_4$ ) or germane ( $\text{GeH}_4$ ) in the presence of phosphene ( $\text{PH}_3$ ) or diborane ( $\text{B}_2\text{H}_6$ ). Recently the group at Harvard University, [W. Paul *et al.*, *Solid State Commun.* **20**, 969 (1976)] demonstrated that sputtered films could also be doped. At the Conference M. Hirose, M. Taniguchi, and Y. Osaka (Hiroshima Univ., Japan) reported that films made by thermal decomposition of silane can have densities of states in the gap sufficiently low that they can be effectively doped. It is even possible that films rendered amorphous by ion bombardment can be doped (G. Miller and S. Kalbitzer, Max-Planck Institut, Heidelberg). It now appears that the method of preparation is not as critical as originally supposed, and it is not at all clear at present which method, if any, will ultimately produce commercially viable devices.

As most of the films are prepared from silane or germane, the role of hydrogen in producing the observed electrical properties of these films has been hotly debated (see *ESN* 31-3:81 on the Chelsea Amorphous Semiconductors meeting, 20-21 December 1976). We now know that the amount of hydrogen in these films is substantial ( $\sim 10$ -20 at.%), and many authors have begun to recognize this fact explicitly by referring to the materials as Si-H alloys,  $\text{SiH}_x$  films or hydrogenated-Si films (W. Paul, H. Fritzsche, as well as M. Bermejo, M. Brodsky, and M. Cardona from the Max-Planck Institut, Stuttgart and the IBM Watson Research Center, Yorktown Heights). In his opening invited talk Fritzsche presented evidence from both his own studies and those of Brodsky *et al.* for at least two types of bonding sites for the hydrogen. Whether the hydrogen plays an active or passive role in determining the density of states in the gap and the transport properties is still a controversial matter. The Dundee group suggests that the hydrogen is primarily a passive constituent and supports this contention with various annealing arguments, while the IBM group favors the active hypothesis and suggests spectroscopic and analytical chemical evidence in support of their view. The precise role of hydrogen in these films remains a very significant question. Evidence that nearly all of the hydrogen is bonded into the network was presented by Bermejo *et al.* who cited analyses of the infrared vibrational absorption bands observed in these films as compared to those observed in various Si-H gases (silanes, disilanes, etc.).

Another significant controversy at the meeting concerned absolute numbers for the density of states within the energy gap in the amorphous Si-H and Ge-H films and the accuracy of the field-effect measurements that are used to obtain these numbers. The Dundee group suggested that the field-effect values are good to within a factor of three, but other



experimenters (G.H. Döhler and M. Hirose from the Max-Planck Institut, Stuttgart), using films obtained from the University of Marburg (J. Stuke), were unable to reproduce even the shape of the density-of-states curves determined at Dundee. As is often the case in matters of controversy, the discussion quickly degenerated into a series of rather esoteric exchanges on specific details of the experimental procedures and data-reduction schemes. The role of surface states in determinations of the density of states was also a controversial point with J.C. Knights (Xerox Research Center, Palo Alto) suggesting that these states are important and Spear contending that they are not. All of these arguments make estimates of the efficiency of the doping process, which is a most important device consideration, highly controversial. Spear suggested that the doping is "not all that inefficient," but since his conclusion was based upon one interpretation of the field-effect measurements, his view was contested by several other groups (Xerox Research Center and IBM, among others). The general outcome of the entire discussion was well summarized by Fritzsché who noted clear evidence for the presence of too few experiments and too many parameters. If one fact emerged from this particular discussion, it was that there are a great many well-respected research groups all very interested in the details of the density of states within the gap in Si-H and Ge-H films (Dundee, Sheffield, IBM in Yorktown Heights, Xerox in Palo Alto, Marburg, Max-Planck Institutes in Stuttgart and Heidelberg, Chicago, Harvard, Hiroshima, and RCA in Princeton among others).

The meeting contained many papers concerned with specific experimental probes of the states in the gap in amorphous tetrahedrally coordinated films. In his invited talk, Spear discussed the temperature dependence of the Hall effect, thermoelectric power and photoconductivity as functions of doping. Other authors discussed various transport experiments in these films (Beyer *et al*, Marburg; Allen *et al*, Dundee; Anderson *et al*, Harvard). Photoluminescence results were presented by D. Engemann *et al* (Univ. of Marburg), by T.S. Nashashibi *et al* (Univ. of Sheffield), by Brodsky and J.J. Cuomo (IBM, Yorktown Heights) and by J.I. Pankove and Carlson (RCA, Princeton). Both the PL efficiency and the shape of the PL spectrum change with hydrogen content in somewhat complicated fashions. In addition, the PL efficiency is reduced on doping with boron or phosphorous. The PL center is associated with the hydrogen, but the exact nature of the center is still unknown.

In an invited presentation, Stuke reviewed the ESR results in amorphous Si-H and Ge-H films and in some Si-Ge alloys. The talk mainly concerned the behavior of the spin density, the line width and the g-value (resonant field position) as functions of preparation conditions, doping, and electron irradiation. In boron-doped amorphous Si three ESR lines are observed, and Stuke presented some evidence for associating the broadest line with the presence of the boron. Similar ESR centers are created in the initial preparation of the films (before annealing) and by electron bombardment of annealed films. This situation is in marked contrast to the optically induced ESR centers in chalcogenide glasses which differ from those created

by electron bombardment. In fact, most of the properties of the ESR and photoinduced ESR centers in amorphous Si and Ge are quite different from those of the optically induced centers in the chalcogenide glasses (see Section A of this report).

In two separate papers Knights and D.K. Biegelsen (Xerox Research Center, Palo Alto) described the dependences of the optically induced ESR in amorphous Ge and Si on doping, temperature, and light intensity. It was suggested that the existence of very low equilibrium densities for heavily doped samples coupled with the existence of high optically induced spin densities indicated the presence of negative-effective correlation energies for the diamagnetic-gap states similar to the picture suggested for the chalcogenides by N.F. Mott. J.R. Pawlik (Harvard Univ.) and Paul also discussed ESR and optically induced ESR in similar materials.

At low-spin concentrations the ESR line shapes become asymmetric (R.S. Title *et al*, IBM, Yorktown Heights). It was suggested that this line shape is best explained by electrons in disordered divacancies or multivacancies. At higher concentrations motional effects become important, and these processes were analyzed by B. Movaghar and L. Schweitzer (Univ. of Marburg) in terms of a distribution of relaxation times for the ensemble of unpaired electrons.

Of all of the papers presented on the doped amorphous Si and Ge films only two could reasonably be described as devoted to device applications. In one of these C.R. Wronski (RCA, Princeton) and Carlson described the electronic properties of the amorphous Si used in efficient (6%) solar cells [D.E. Carlson and C.R. Wronski, *Appl. Phys. Lett.* **28**, 671 (1976)]. Significant differences between the properties of these films and those of the Dundee group were reported. In the second paper devoted to device applications, R.W. Griffith (Argonne National Laboratory, Chicago) discussed the tailoring of the absorption edge in amorphous Si to optimize the absorption of the solar spectrum and still maintain infrared transparency.

#### E. THERMAL AND VIBRATIONAL PROPERTIES

The session on thermal and vibrational properties was highlighted by the invited paper of K. Dransfeld (Max-Planck Institute, Stuttgart). The paper was coauthored by S. Hunklinger. The tutorial, yet up-to-date, lecture was one of the most successful invited talks of the meeting. Dransfeld outlined the history of the anomalous low-temperature thermal properties of disordered solids, in which the group under R.O. Pohl (Cornell Univ.) has played a considerable role. These measurements demonstrated the existence of low-energy states that apparently are unique to the amorphous state. Although the thermal measurements indicate the number of such states ( $\sim 10^{17}$  per  $\text{cm}^3$  between 0 and 1 K), they cannot provide detailed information about the physical nature of the states. Such information can be obtained from the study of the interaction of high-frequency



sound waves with the low-energy states. These studies were initiated by the discovery a few years ago by B. Golding *et al* (Bell Laboratories) and by S. Hunklinger *et al* (Max-Planck Institute, Stuttgart) that the acoustic attenuation in glasses at low temperatures (<1 K) saturates at sufficiently high acoustic-power levels. This discovery provided the first conclusive experimental evidence that the low-energy excitations could be described in terms of two-level states, whose existence had been proposed earlier by P.W. Anderson and coworkers (Bell Laboratories) as well as by W.A. Phillips. Since these initial discoveries, the groups at MPI, Stuttgart and Bell Laboratories have determined critical parameters of the two-level systems. The new data include the measurements of the lifetimes of the two-level systems in their excited states (analogous to the  $T_1$  spin-lattice relaxation time for a spin system) and the phase-memory time (analogous to the  $T_2$  spin-spin relaxation time). Measurements of these parameters are best obtained by means of acoustic phonon-echo techniques (B. Golding and Graebner). In this measurement two acoustic pulses are applied within a time interval of  $t \sim 1 \mu\text{sec}$ , with a coherent emission of an acoustic pulse a time  $\tau$  later. This is a remarkable observation, considering the disordered state of these solids, that promises to become an important tool in the study of the elementary lattice excitations of amorphous materials.

Dransfeld further reported that the interaction between two-level states has been studied using an acoustic pulse at fixed frequency, followed by a probing pulse of different frequency. It was found in experiments by W. Arnold *et al* (MPI, Stuttgart) that the probing pulse encountered a saturated medium far away ( $\geq 50 \text{ MHz}$ ) from the initial  $\sim 1\text{-GHz}$  pulse. This result indicates coupling between the two-level modes mediated by the lattice. Similar information can be obtained from measurements of the temperature-dependent NMR relaxation rate, as had been discussed previously by T.L. Reinecke and K.L. Ngai (Naval Research Laboratory, Washington, DC).

The final portion of Dransfeld's lecture described the absorption of electromagnetic waves in glasses. Again only the low-temperature regime (<10 K) was considered. It was shown that the temperature variation of the dielectric constant is analogous to the temperature variation of the speed of sound. However, in contrast to the insensitivity of the acoustic attenuation to impurities, the rf absorption is strongly enhanced with increasing impurity concentration. The magnitude of the optical-dipole moment for the impurity containing glass can lead to a measure of the size of the two-level excitations. For the case of  $\text{OH}^-$  in  $\text{SiO}_2$ , M. Von Schickfus and S. Hunklinger (MPI, Stuttgart) deduce that the low-energy excitations are smaller than  $20 \text{ \AA}$ . These observations were discussed in detail in a contributed talk by Schickfus later in the session. Other contributed papers on the topic of low-temperature measurements in amorphous solids included a study of the dielectric response of  $\alpha\text{-Si}$  between  $10^2$  and  $10^5$  by B. Golding *et al*, and measurements of the specific heat of  $\alpha\text{-germanium}$  by A. Couz-Uribe and J. Trefuy (Wesley Univ., CT).

The ultrasound experiments described by Dransfeld and Golding require low temperatures such that at their experimental frequencies ( $\sim 1$  GHz) generally  $\hbar\omega \gg kT$ . In this limit the quantum character of the low-frequency excitations is manifested in their unique dielectric and acoustic responses. In the opposite limit  $kT \gg \hbar\omega$ , which is generally satisfied at higher temperatures  $>10$  K in the microwave regime, other lattice excitations as well as relaxation processes involving two-level modes come into play. In a contributed paper to this session U. Strom, D. Schafer, and P.C. Taylor (Naval Research Laboratory) have interpreted the pronounced temperature-dependent microwave absorption (between 10 and 300 K) observed in glasses in terms of the optical excitation of highly damped lattice modes. Such modes are not describable in terms of the usual Debye theory of lattice excitations. Their precise nature is not understood. However, a possible interpretation is that thermally excited two-level modes will be surrounded by a "cloud" of lattice distortions which can range from highly damped and localized modes to Debye-like long-wavelength sound waves. Another contributed talk dealing with higher-temperature ( $>10$  K) lattice excitations was by F. Al-Berkdar *et al* (Heriot-Watt Univ., Edinburgh) and presented by P.C. Taylor. This talk discussed the far-infrared absorption observed in amorphous arsenic ( $\alpha$ -As) in terms of a plausible phenomenological model. It was concluded that  $\alpha$ -As differs markedly from other amorphous solids in that there is a considerably reduced disorder-induced coupling to a Debye-like  $\omega^2$  phonon density of states. This suggests that the low-frequency vibrational properties of  $\alpha$ -As differ from those of other materials. Indeed, its low-temperature thermal properties are quite unlike those of most amorphous solids in that the usual linear-temperature contribution to the specific heat is not observed.

#### F. UNUSUAL SEMICONDUCTOR MATERIALS

The semiconductor community has always had a broad view of the field of its concern. For instance, insulating solids have, on occasion, been included as large band-gap semiconductors. In the present conference the organizers were careful to allow for expansion of the field by including sessions on oxide glasses, organic materials, and liquid semiconductors. Certainly these materials are different from the more usual amorphous semiconductors and allow experimental approaches that are not possible with the more conventional materials.

In an invited paper Dr. M.J. Weber (Lawrence Livermore Laboratory) described experiments on the fluorescence of ions in oxide glasses. Because of the variations in the number of nearby ions, their type, and the strength of their interactions, the fluorescence of ions in glass excited by broadband light is broadened beyond the spectrum of the same ions in corresponding crystals. This effect can be reduced by using short laser pulses of very narrow width to excite ions in a small range of configurations. By varying the exciting wavelength, changes in the emission spectrum and decay times can be correlated with the expected changes in



environment of the fluorescent ion. In particular, glasses of varying composition of  $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ , with about 1% of  $\text{Eu}^{3+}$  have been studied. The  $\text{Eu}^{3+}$  ions are excited into the  $^5\text{D}_0$  and  $^5\text{D}_2$  states. Fluorescent emission arises from transitions from the  $^5\text{D}_0$  state to levels of the  $^7\text{F}$  multiplet and gives an eight-line spectrum. Line emission from other transition and post-transition metal ions in glasses suitable for line narrowing is rare. What is required are pairs of levels with separations that are independent of the crystal field. Weber suggests that  $\text{M}_0^{3+}$  may be a possible candidate.

Studies have also been made of multiphonon transitions in these glasses using the fluorescence decay time of the rare-earth emission as a measure. The rates of these processes appear to be determined primarily by the size of the energy gap rather than the particular electronic states or phonon modes that are involved.

A particular study of a rare-earth transition in oxide glasses and crystals at liquid-helium temperature showed that the linewidth in the glass was significantly larger and had a different temperature dependence. The increased broadening in the glasses was attributed to motions associated with the low-frequency excitation measurements of virtually all glasses as mentioned earlier in Section E. This detailed spectroscopy of fluorescent ions in glass is new and developing rapidly. It may well become an important tool in a wide range of materials as well as the oxide glasses.

Dr. J. Mort (Xerox Webster Research Center, NY) described photoelectric properties of disordered organic solids. He pointed out that these amorphous materials might be expected to have fundamental differences compared with the usual amorphous semiconductors. These differences arise from the weak molecular binding in organic solids that leads to energy bands that are so narrow and mobilities so low that band theories of transport become questionable or invalid. Instead, a more natural way to think of conduction in disordered organics is that charge transfer occurs between neighboring molecules.

Mort described experiments on organic films using the time-of-flight technique in which charge is generated by a 5-nsec pulse of 3371-Å light and then swept across a 10 to 20-μm thick film (see Section B). The films were basically of a polycarbonate polymer, General Electric LEXAN, doped with varying amounts of N-isopropyl carbazole (NIPC) and triphenylamine (TPA). The LEXAN itself does not show charge displacements when irradiated. Both NIPC and TPA lead to hole conductivity when included in the LEXAN. The shape of the current pulses and the dependence of the charge on the doping concentrations strongly support a transport mechanism involving hops between a random array of the dopant molecules. Analysis of the data indicates a localization radius of 1.5 Å for the NIPC molecule. More complex experiments involving double doping and photosensitization can be similarly interpreted. These experiments emphasize that conduction

in amorphous organic materials involves a simple charge transfer between closely spaced molecules.

In conclusion, it should certainly be reported that the nearly 350 attendees at the Conference owe a debt of gratitude to the organizing committees for the fine arrangements and the well-worked-out details. In particular, the presence and spirit of Professor Sir Nevill Mott, Chairman of the International Committee, enlivened all of the Conference affairs.